280. *The Relative Affinities of an Amine, an Organic Phosphine, and a Sulphide for Cadmium Ion.*

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The stability constants of the metanilate, 3-sulphotriphenylphosphine, and 4-sulphodiphenyl sulphide ions with cadmium ion have been determined. The first stability constants (K_1) are all smaller than their analogues with silver ion and the difference is very marked in the case of the phosphine. We interpret this great weakening of the phosphine complexes on passing from silver to cadmium to mean that the strength of dative π-bonding from the metal to ligand falls sharply at the end of the transition series of metals.

We [1,2] have already measured the stability constants of a number of similar organic derivatives of nitrogen, phosphorus, arsenic, oxygen, sulphur, and selenium for silver(I) in aqueous solutions and now we describe an extension of that work to cadmium(II) ion. The constants were determined by titrating a solution of cadmium perchlorate with a solution of the ligand, a cadmium amalgam electrode being used to measure the change in concentration of the cadmium ion as the titration proceeded. The experimental method, the method of calculation, and the meanings of the symbols used are given in reference 1.

The cadmium complexes are very weak and their stability constants could not be accurately determined. The greatest change in e.m.f. due to the formation of complexes in any of these experiments was only 13·2 mv. The constants which we have determined are listed in Table 1. It is to be noted that the stabilities of the second complex in the case of the phosphine, and of the third in the case of the sulphide, are enhanced relatively to those of the lower complexes. The accuracy of the determinations is not sufficient to warrant any discussion of the ratios K_1/K_2 except to point out that this ratio in the case of the phosphine appears to be exceptionally low (0·027).

Attempts to obtain the stability constants of the 4-sulphodiphenyl selenide ion failed.

Table 1. *Stepwise stability constants, K (in l. mole*$^{-1}$*), and gross stability constants,* β, *of the ligands,* L, *with cadmium ion at an ionic strength I and* 25°.

L	I	K_1	K_2	β_2	β_3
$3\text{-}NH_2\cdot C_6H_4\cdot SO_3^-$	1·0	1·8	2	3·5	—
$3\text{-}PPh_2\cdot C_6H_4\cdot SO_3^-$	0·1	≈8	$\gtrsim$300	2500	—
$4\text{-}SPh\cdot C_6H_4\cdot SO_3^-$	0·2	4·7	—	<10	1100

Metal ions which we [1] have designated type (*b*) form their strongest complexes with the second or a subsequent co-ordinating atom rather than with the first from each Group of co-ordinating atoms in the Periodic Table. They probably owe this peculiarity, which distinguishes them from the commoner type (*a*) metal ions, to their ability to release electrons to form dative π-bonds with co-ordinating atoms having suitable orbitals to receive them.[3] The second and subsequent co-ordinating atoms, but not the first, in each Group have vacant *d*-orbitals which can receive electrons to form π-type bonds. The electrons are usually supplied from *d*-orbitals of the metal ion and so class (*b*) character is most marked when the metal ion has filled *d*-orbitals and low ionic charge. Silver(I) has a greater class (*b*) character than any other acceptor ion or molecule, the stabilities of whose complexes with a large range of co-ordinating atoms have been investigated quantitatively.[2] Cadmium(II) is isoelectronic with silver(I), but its ionic charge is twice as great. We should therefore expect the electrons in cadmium(II) to be more strongly held, and particularly its *d*-electrons will not be so readily available for dative π-bonding. Thus the type (*b*) character of cadmium(II) should be less than that of silver(I).

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[1] Ahrland, Chatt, Davies, and Williams, *J.*, 1958, 264.

[2] *Idem, J.*, 1958, 276.

[3] Chatt, *Nature*, 1950, **165**, 637; Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, **332**; Jaffe, *J. Phys. Chem.*, 1954, **58**, 185.

Our measurements confirm this view. In Table 2 the first stability constants, K_1, of a representative selection of unidentate ligands with silver(I) and cadmium(II) are given for comparison. Cadmium is evidently near the border between classes (*a*) and (*b*). Its first constants, K_1, with all except the acetate and the fluoride ion, are lower than in the silver series. Those of the amine, sulphide, chloride, and bromide, where we consider dative π-bonding to be absent or weak, even with silver(I), are reduced only by a factor of 10—100 in passing from silver(I) to cadmium(II). On the other hand, the stability constants, K_1, of the phosphine and iodide ion, where d_π-bonding with silver ion is very strong,[2] are reduced by factors of about 10^6. It is evident that the capacity of the metal ions to form strong dative π-bonds falls sharply at the end of the transition series of metals.

Two causes can be advanced for the exceptional behaviour of the acetate and the fluoride ion: (*a*) that the M–O and M–F bonds are largely electrostatic in character and so the anionic ligand is held more strongly by the bipositive cadmium ion than by the isoelectronic but unipositive silver ion; (*b*) that the lone-pair repulsion between the filled d_{xy}-type of orbitals in the metal ion and filled *p*-orbitals of the oygen and fluorine atoms is greater with silver(I) than with cadmium(II) where the greater nuclear charge will contract the *d*-orbitals. Doubtless both of these effects operate, and perhaps entropy effects as well.

TABLE 2. *The first stability constants* K_1(Ag) *and* K_1(Cd) *for a selection of unidentate ligands with silver and cadmium ions at ionic strength* I ($NaClO_4$) *and* 25°.*

Ligand	I	log K_1(Ag)	I	log K_1(Cd)	Ligand	I	log K_1(Ag)	I	log K_1(Cd)
NH_3	2·0	3·20 [a]	2	2·65 [a]	F^-.........	1·0	−0·32 [e]	1·0	0·46 [f]
$3\text{-}NH_2{\cdot}C_6H_4{\cdot}SO_3^-$	1·0	1·23 [b]	1·0	0·26 [d]	Cl^-	5	3·08 [g]	3	1·59 [h]
$3\text{-}PPh_2{\cdot}C_6H_4{\cdot}SO_3^-$	0·1	8·15 [b]	0·1	~0·9 [d]	Br^-	0	4·38 [i]	0	2·23 [j]
$CH_3{\cdot}CO_2^-$	3·0	0·37 [l]	3·0	1·30 [l]				3	1·76 [h]
$4\text{-}SPh{\cdot}C_6H_4{\cdot}SO_3^-$ ...	0·2	1·67 [c]	0·2	0·67 [d]	I^-	4	8·13 [k]	3	2·08 [h]

* Many determinations of the constants for the halide ions are available in the literature. These were chosen as giving the best comparison between silver and cadmium. Vertical comparisons are not so good because of differences in ionic strength.

[a] At 30° in NH_4NO_3; J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," Haase and Son, Copenhagen, 1941, pp. 134, 160. [b] Ref. 2. [c] Ref. 1. [d] This work. [e] Leden and Marthèn, *Acta Chem. Scand.*, 1952, **6**, 1125. [f] Ref. 4, p. 49. [g] Leden, *Svensk kem. Tidskr.*, 1953, **65**, 88. [h] Leden, *Z. phys. Chem.*, 1941, *A*, **188**, 160. [i] Berne and Leden, *Z. Naturforsch.*, 1953, **8**, *a*, 719. [j] Kivalo and Ekari, *Suomen Kem.*, 1957, *B*, **30**, 116. [k] Leden and Parck, *Acta Chem. Scand.*, 1956, **10**, 535; Leden, *ibid.*, p. 812. [l] At 20°; Leden, *Svensk kem. Tidskr.*, 1946, **58**, 129; see also ref. 4, p. 89.

EXPERIMENTAL

The preparations of the sulphonated ligands used in these investigations have been described.[1, 2] The constants were determined by the same method as those of the sulphonated amines, sulphide, and selenide with silver ion.[1] Cadmium amalgam (10%) electrodes were used in place of the Ag–AgCl electrodes, and cadmium perchlorate in place of silver perchlorate. The cell in which the measurements were made was similar to that used in the silver experiments, but the amalgam electrode half-cell had two small pockets in the base connected by sealed-in platinum contacts to the outer circuits, and two manually operated platinum-wire stirrers through the top of the cell and capable of reaching into the pockets. The pockets were used to contain the amalgam ($\frac{1}{2}$—1 c.c.), and the stirrers to clean its surface whenever contamination was suspected. The amalgam was prepared and used as described by Leden.[4] The e.m.f.s of the cells were very stable and reproducible to 0·2—0·3 mv.

The experimental results are given in Tables 3—5. C_L' is the concentration of ligand solution used to titrate the cadmium perchlorate solution of ionic strength I ($NaClO_4$). C_L is the actual concentration of ligand in the half-cell, and E_M the change in e.m.f. of the cell caused by complex formation between the ligand and cadmium ion. X, X_1, etc., are functions defined in the appendix to reference 1. In all the experiments complex formation was so weak that E_M was virtually independent of the initial concentration of cadmium ion C_M' at the concentrations used.

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[4] Leden, "Potentiometrisk Undersöking av Några Kadmiumsalters Komplexitet," Gleerupska Univ.-Bokhandeln, Lund, 1943, p. 34.

Sodium Metanilate.—Titrations were performed at $C_M' = 20$ mM and 5 mM. Complex formation was so weak that even at $C_L = 500$ mM the ligand number $\bar{n}$ did not exceed 1·5 (Table 3).

TABLE 3. *The system cadmium ion–metanilate ion.*

($C_L' = 1$M; $I = 1$M)

$C_L = [L]$	E_M	X	X_1	X_2	$C_L = [L]$	E_M	X	X_1	X_2
38·5	0·9	1·072	1·9	—	285·7	7·5	1·790	2·77	3·4
62·5	1·5	1·125	2·0	—	318	8·3	1·908	2·86	3·3
90·9	2·3	1·195	2·14	—	348	9·2	2·048	3·01	3·5
117·6	3·0	1·265	2·26	—	400	10·6	2·285	3·22	3·6
166·7	4·3	1·398	2·39	3·5	444	11·7	2·490	3·36	3·5
210·5	5·5	1·534	2·54	3·5	500	13·2	2·798	3·60	3·6
250·0	6·5	1·658	2·63	3·3					

$\beta_1 = K_1 = 1{\cdot}8 \pm 0{\cdot}2$ l. mole^{-1}; $\beta_2 = 3{\cdot}5 \pm 0{\cdot}2$ l.^{2} mole^{-2}; $K_2 = 2$ l. mole^{-1}.

Sodium Salt of 3-*Sulphotriphenylphosphine.*—This ligand caused a precipitate at $C_M' > 2$ mM. Titrations were therefore performed at $C_M' = 1$ and $C_M' = 0{\cdot}5$ mM. The use of these low concentrations set the limits to the accuracy of the experiment (Table 4).

TABLE 4. *The system cadmium ion*–3-*sulphotriphenylphosphine ion.*

($C_L' = 0{\cdot}03$M; $I = 0{\cdot}1$M)

$C_L = [L]$	E_M	X	X_1	X_2	$C_L = [L]$	E_M	X	X_1	X_2
1·88	0·5	1·040	21	—	9·57	3·1	1·273	28·5	2100
3·54	0·6	1·048	14	—	10·44	3·5	1·312	29·9	2100
5·01	0·8	1·064	13	—	12·00	5·0	1·476	39·6	2600
6·33	1·0	1·081	13	—	13·32	5·8	1·570	42·8	2600
7·50	1·7	1·141	18·8	—	15·00	6·9	1·710	47·3	2600
8·58	2·2	1·187	21·8	—					

$\beta_1 = K_1 \approx 8$ l. mole^{-1}; $\beta_2 = 2500$ l.$^{-2}$ mole^{-2}; $K_2 \approx 300$ l. mole^{-1}.

Sodium Salt of 4-*Sulphodiphenyl Sulphide.*—Titrations were performed at $C_M' = 20$, 10, and 5 mM (Table 5).

TABLE 5. *The system cadmium ion*–4-*sulphodiphenyl sulphide ion.*

($C_L' = 0{\cdot}2$M; $I = 0{\cdot}2$M)

$C_L = [L]$	E_M	X	X_1	X_2	X_3	$C_L = [L]$	E_M	X	X_1	X_2	X_3
7·69	0·5	1·040	5·2	—	—	57·1	4·8	1·453	7·9	56	980
12·50	0·8	1·064	5·1	—	—	63·6	5·8	1·570	9·0	68	1070
18·2	1·2	1·098	5·4	—	—	69·6	6·9	1·710	10·2	79	1130
23·5	1·6	1·134	5·7	—	—	80·0	8·7	1·968	12·1	93	1160
33·3	2·3	1·195	5·9	36	1100	88·9	10·3	2·231	13·8	100	1120
42·1	3·1	1·273	6·5	43	1020	100·0	12·3	2·608	16·1	114	1140
50·0	3·9	1·355	7·1	48	960						

$\beta_1 = K_1 = 4{\cdot}7 \pm 0{\cdot}5$ l. mole^{-1}; $\beta_2 < 10$ l.^{2} mole^{-2}; $\beta_3 = 1100 \pm 200$ l.^{3} mole^{-3}.

Sodium Salt of 4-*Sulphodiphenyl Selenide.*—Steady cell potentials were not obtained with this ligand. It appeared to attack the surface of the amalgam electrode because stirring the amalgam caused a change in potential of 0·25 mv, and without stirring the potentials fluctuated irregularly. No constants were obtained.

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